

AD-A079 688

DEFENCE RESEARCH ESTABLISHMENT OTTAWA (ONTARIO)  
PULSE CAPABILITY OF THE AIRI LEAD CHLORIDE ELECTRODE.(U)  
NOV 79 G J DONALDSON, W D BARNES

F/G 10/3

UNCLASSIFIED

DREO-TN-79-26

NL

for  
AD  
A079688



END  
DATE  
FILMED  
2-80

DDC

**LEVEL**

DISTRIBUTION  
ILLIMITED

RESEARCH AND DEVELOPMENT BRANCH  
DEPARTMENT OF NATIONAL DEFENCE  
CANADA

AD A 079688

**DEFENCE RESEARCH  
ESTABLISHMENT OTTAWA**

DDO  
RECEIVED  
JAN 12 1980  
REGULATED  
E

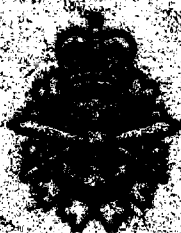
DRED TECHNICAL NOTE NO. 79-26  
DRED TN 79-26

**PULSE CAPABILITY OF THE AIR  
LEAD CHLORIDE ELECTRODE**

by

**G.J. Donaldson and W.D. Barnes**

DDC FILE COPY



This document has been approved  
for public release and sale  
distribution is unlimited

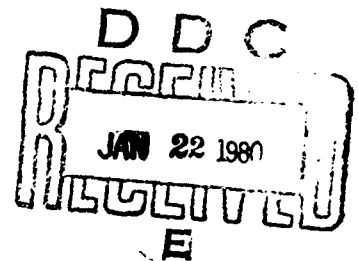
80 1 14 10

**CAUTION**

This information is furnished with the express understanding  
that proprietary and patent rights will be protected.

RESEARCH AND DEVELOPMENT BRANCH

DEPARTMENT OF NATIONAL DEFENCE  
CANADA



DEFENCE RESEARCH ESTABLISHMENT OTTAWA

TECHNICAL NOTE NO. 79-26

4  
11 JAN 21 1980

PULSE CAPABILITY OF THE AIRI LEAD CHLORIDE ELECTRODE,

by

126 G.J. Donaldson and W.D. Barnes

Chemical Sources Section  
Energy Conversion Division

1215

11  
NOVEMBER 1979  
OTTAWA

404-16

UNCLASSIFIED

TABLE OF CONTENTS

	<u>Page</u>
<u>ABSTRACT</u> . . . . .	v
<u>RÉSUMÉ</u> . . . . .	vi
<u>INTRODUCTION</u> . . . . .	1
<u>EXPERIMENTAL</u> . . . . .	2
GENERAL METHOD. . . . .	2
PULSE DISCHARGE EXPERIMENTS . . . . .	3
<u>RESULTS AND DISCUSSION</u> . . . . .	5
CELL INTERNAL RESISTANCE. . . . .	5
PULSE PERFORMANCE OF LEAD CHLORIDE VERSUS SILVER CHLORIDE . . . . .	6
LEAD CHLORIDE CATHODES. . . . .	8
<u>INFLUENCE OF STEADY DISCHARGE RATE ON PULSE BEHAVIOUR.</u> . . . . .	8
<u>INFLUENCE OF PULSE LOAD ON PULSE BEHAVIOUR</u> . . . . .	10
<u>CONCLUSION</u> . . . . .	15
DESIGN OF A Mg/PbCl <sub>2</sub> PULSE BATTERY. . . . .	15
<u>REFERENCES</u> . . . . .	16

UNCLASSIFIED

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability of _____	
Dist	Archival Special
A	

UNCLASSIFIED

ABSTRACT

The objective of the study was to evaluate the pulse discharge performance of lead chloride electrodes for the active sonobuoy battery application. Experimental work was carried out using Mg/PbCl<sub>2</sub> cells which were pulse discharged in 3.25% artificial seawater at ambient temperatures (22°-25°C). Pulses of 100 milliseconds duration were applied every ten seconds by switching the cells from their steady discharge load to the pulse discharge load.

It was found that the steady rate of discharge had to be maintained at about 5-10 mA cm<sup>-2</sup> in order to permit a sufficiently rapid response to the application of the pulse load without unduly sacrificing electrode capacity. The Mg/PbCl<sub>2</sub> cell was required to accept a pulse load greater than the steady load by a factor of approximately 25; the resulting loss of cell output voltage was about 0.6 volts. Although Mg/AgCl cells suffer about the same loss of output, the levels are about 0.5 volts higher in both steady and pulsed discharge modes than those for the Mg/PbCl<sub>2</sub> cell.

A further serious disadvantage of the PbCl<sub>2</sub> electrode is its greater size and weight compared to silver chloride. Lead chloride electrodes do not offer a performance advantage over silver chloride for active sonobuoy batteries. In view of the impending conversion of all types of sonobuoys to the use of lithium batteries in about five to eight years time there is little advantage to pursuing the development of the lead chloride electrode for such applications.

UNCLASSIFIED

NON-CLASSIFIÉ

### RÉSUMÉ

La présente étude vise à évaluer le rendement en régime de décharge pulsé d'électrodes au chlorure de plomb destinées à être utilisées dans les batteries pour bouées sonores actives. Les travaux expérimentaux ont été effectués avec des cellules Mg/PbCl<sub>2</sub> déchargées en régime pulsé dans de l'eau de mer artificielle à 3.25% en conditions de température ambiante (22°C-25°C). Des impulsions d'une durée de 100 millisecondes étaient produites en passant, à toutes les dix secondes, d'un régime de décharge normal à un régime de décharge pulsé.

Nous avons constaté qu'il fallait maintenir la décharge en régime normal à une densité de courant d'environ 5-10 mA cm<sup>-2</sup> afin d'obtenir une réaction suffisamment rapide à la décharge en régime pulsé sans sacrifier inutilement le rendement de l'électrode. Il fallait que la cellule Mg/PbCl<sub>2</sub> puisse fournir en régime pulsé une décharge quelque 25 fois supérieure à la décharge en régime normal; il en résultait une diminution d'environ 0.6 volt au niveau de la tension de sortie. Les cellules Mg/AgCl accusaient la même perte de tension, mais les potentiels de décharge en régime normal et en régime pulsé étaient d'environ 0.5 volt plus élevés que ceux d'une cellule Mg/PbCl<sub>2</sub>.

La grandeur et la pesanteur des électrodes au PbCl<sub>2</sub> constituaient un autre grave inconvénient par rapport aux électrodes au chlorure d'argent. Les électrodes au chlorure de plomb n'offraient aucun avantage réel par rapport aux électrodes au chlorure d'argent. Tout travail ultérieur portant sur la mise en point d'électrodes au chlorure de plomb destinées à ce type d'application ne serait guère avantageux, car d'ici 5-8 ans toutes les bouées sonores seront dotées de batteries au lithium.

NON-CLASSIFIÉ

### INTRODUCTION

At present active sonobuoys constitute about twenty percent of all sonobuoys used annually by the Canadian Forces. This proportion is expected to increase yearly, but in the meantime newer types of active buoys are being developed, including the command-active sonobuoy (1).

An active sonobuoy (unlike the passive listening variety of buoy) produces an ultrasonic pulse for the detection of underwater targets. This function requires an electrical power source capable of generating electrical impulses, hereafter to be called simply "pulses". The power source now in use is a seawater-activated battery in which the anode is a magnesium alloy and the cathode a silver chloride electrode. These batteries are admirably capable of meeting the electrical specifications, but for reasons of cost lead chloride has replaced silver chloride in the passive sonobuoy. It was therefore important to assess the pulse discharge capability of lead chloride. In the event active sonobuoys require batteries of much greater energy content than at present, the cheaper lead chloride would offer a significant economy as has been the case with the passive type of sonobuoy.

It was decided to evaluate a lead chloride electrode developed through DREO contracts with the Atlantic Industrial Research Institute (AIRI). This material has been examined for use in passive sonobuoys and is suitable for that application (2,3), if the required duration of discharge does not exceed five to six hours. Further development is currently underway to make the eight-hour electrode and is being supported by government financial assistance to SAFT Batteries of Canada, Limited. SAFT is planning to go into the production of lead chloride sonobuoy batteries in Canada for a worldwide market.



## EXPERIMENTAL

### GENERAL METHODS

The plan was first to characterize the pulse discharge behaviour of individual magnesium/lead chloride cells in an electrolyte of artificial seawater. After obtaining data at ambient temperatures (20°-25°C) in normal salinity electrolyte (i.e. 3.25% by weight sodium chloride in water) pulsing would be done over a range of temperatures and salinities common to Canadian oceanic waters. Following this, the cell results were to be used for designing multi-cell batteries which would conceivably meet the pulse discharge profile for an active sonobuoy.

A general specification was chosen as best representing the electrical requirements for an active sonobuoy battery (1). The specification was reduced to a very simple form in order to proceed with a preliminary investigation of the pulse discharge performance of the AIRI lead chloride electrode. Essentially, the battery output during the steady (i.e. non-pulse) discharge period is nominally 40 volts across a 33.3 ohm load. Electrical impulses of 100 milliseconds (ms) duration are required every 10 seconds. During this pulse the output across the pulse load of 1.3 ohm must not fall below 18.5 volts. The total discharge capacity is not relevant for the present work, but in-service active sonobuoys have an operating time from 30 min to 90 min.

The most significant factor in terms of pulse discharging of cells is the ratio (f) of the steady discharge load ( $R_s$ ) to the pulse discharge load ( $R_p$ ):

$$f = R_s/R_p = \frac{33.3\Omega}{1.3\Omega} = 25.6 \quad [1]$$

Hereafter f will be referred to as the load ratio. Previous work on the AIRI lead chloride electrode done in this laboratory used shallow pulse discharging, that is, the load ratio was varied from 1.5 to 13.2 (2). The approach adopted in the present study was to vary the load ratio over a much wider range: from 10 to 60, so as to include the actual value  $f = 25.6$  which is relevant to currently used active sonobuoys.

The first part of the work examined how much improvement in

performance could be achieved by decreasing the resistance of the electrolyte path. Secondly, the experimental study involved changing the pulse load ( $R_p$ ) and steady load ( $R_s$ ) simultaneously, keeping a constant load ratio. Here the objective was to determine the best steady discharge rate commensurate with good pulse performance. Finally, a value of  $R_s$  was fixed and the load ratio was varied from 10 to 60 to evaluate cell performance.

All cell discharge experiments were done in 3.25% NaCl (by weight) dissolved in distilled water. Temperatures ranged from 22° to 25°. For the anode the magnesium alloy AZ61 was used (6% aluminum, 1% zinc, remainder magnesium). Prismatic cell construction was employed in which the apparent geometric area of both anode and cathode was 63 cm<sup>2</sup> (i.e. 7.5 cm x 8.3 cm). Interelectrode spacing, unless otherwise specified, was provided by a five-by-five array of vinyl chips 0.05 cm thick. These were cemented to the anode. More detailed descriptions of cell fabrication are given in reference (2).

#### PULSE DISCHARGE EXPERIMENTS

An electronic timer combined with a relay was employed for the introduction of the pulse load resistor into the discharge circuit of the Mg/PbCl<sub>2</sub> cell. The timer was designed to switch to the pulse load for 100 ms every 10 seconds; for the rest of the cycle the steady load ( $R_s$ ) was in the circuit. In those experiments in which very low pulse load resistance was required, say less than 0.06 ohm, the combined resistance of electrical wire leads and the discharge circuit elements had to be kept very small. To do this the pulse load was made from Nichrome alloy strips 0.32 cm wide, 0.051 cm thick (0.0095 ohm cm<sup>-1</sup>) and a sliding contact was used for selecting the length of the resistance strip corresponding to the exact value of the required pulse load. A Leclanché D-cell was used to calibrate the pulse load immediately before an experiment. The electronic timer activated a relay which actually performed the switching function. The test circuit is shown in schematic form in Figure 1. During a pulse the load consisted of the leads to the cells (0.007 ohm), the relay, the strip of Nichrome wire and the shunt (0.010 ohm). It was thus possible to obtain pulse loads as small as 0.03 ohm.

Cells were soldered to electrical leads (30 cm length of No. 12 gauge, stranded copper wire, resistance equal to 0.007 ohm) and connected to the steady load,  $R_s$  before being immersed in the electrolyte. The steady discharge was allowed to proceed for 10-15 minutes before initiating pulsing. The pulse discharging (a 100 ms pulse every 10 s) was continued from this point onwards until the cell output on the steady mode of discharge began to decrease rapidly below approximately 0.95 volts. Experiments generally lasted at least eighty minutes.

The cell EMF during steady discharge was obtained visually from a digital voltmeter (DVM) display at the instant just before a pulse. The cell output was measured at the point where the leads from the cell were connected to the electrical circuitry (points a,b in Figure 1). The current, similarly displayed on a DVM, was obtained from the voltage drop across the shunt (see Figure 1 points b,c). This procedure permitted calculation of the steady load

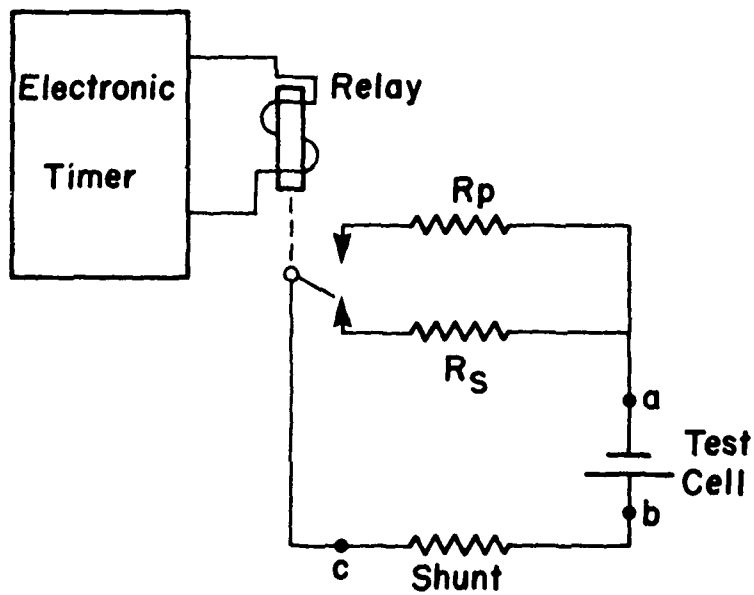


Fig. 1: Schematic diagram of pulse discharge circuit; operation is described in text.

resistance with better than  $\pm 0.005$  ohm precision. During a pulse, the cell voltage and current were displayed on a storage-oscilloscope (Tektronix Model 7623).

Data was sampled approximately every 10 minutes during an experiment. Precision was limited to  $\pm 0.1A$  in the mean pulse current and  $\pm 0.05$  volts for the mean pulse EMF. The average values of cell EMF and current for the pulse discharge were then used to calculate the actual pulse load with a precision of at least  $\pm 0.001$  ohm.

### RESULTS AND DISCUSSION

#### CELL INTERNAL RESISTANCE

One way to improve cell output during a pulse is to decrease the internal resistance of the cell. With this intention an attempt was made to reduce the distance between electrodes by using different materials for spacers.

TABLE I

Spacers for Mg/PbCl<sub>2</sub> Cells

Material	$d^{(a)}$ (cm)	$R_i^{(b)}$ (ohm)
Woven nylon fabric	0.02	0.36
Woven nylon fabric	0.01	0.34
Woven polypropylene	0.013	0.38
Non-woven (mat) polypropylene	0.013	0.34
Vinyl chips, 5 x 5 array	0.05	0.20

(a)  $d \equiv$  separation between electrodes.

(b)  $R_i \equiv$  the apparent internal resistance, measured by the voltage change resulting from a step impulse of current,  $R_i = \left| \frac{\Delta V}{\Delta I} \right|$ .

The results presented in summary form in Table I indicate quite clearly that the only suitable spacers were the vinyl chips. (These were as before (2,3), approximately 0.1 cm square). Even though the fabrics allowed for closer spacing, they in fact excluded a significant volume of ionically conducting electrolyte; the net result was an increase in internal resistance. When inspected following discharge, the anode surface showed evidence of non-uniform wetting when fabric spacers were used. The use of such materials impedes free movement of gas in the cell and leads to the accumulation of reaction products both on the anode and in the porous matrix of the fabric. This again contributes to an increase in resistance. It is very important to maintain a continuous circulation of electrolyte through the cell, even more so in the case of pulsing where a rapid change in output voltage, i.e. a square pulse, is desirable.

It was therefore decided to continue using vinyl spacers with 0.05 cm interelectrode separation. For 3.25% seawater at 25°C with 0.05 cm spacing and 63 cm<sup>2</sup> of electrode surface the electrolyte contribution to the internal resistance is only 0.032 ohm. Electrode separation of less than 0.05 cm was not practical when using the vinyl chip because the cathode which is flexible could touch the anode at some point thus shorting the cell.

Pulsing studies were done at fixed values of  $R_s$  (1.67, 1.00, 0.78 ohm) with three values of  $R_p$  (0.38, 0.24, 0.07 ohm) for a total of nine combinations of  $R_s$  and  $R_p$ . In preliminary experiments a cell was pulsed from a particular value of  $R_s$  to each value of  $R_p$  in succession, first decending to the smallest  $R_p$ , then increasing back to the largest  $R_p$ . This type of pulse experiment yielded irreproducible data. This was due to a variety of causes, but mainly to conditions existing at the anode. The voltage profile of a pulse depends in part on the rate of discharge before the pulse is initiated, because of the roughness of the anode surface, the coverage of the anode by passivating films (of MgO for example) and adherent gas bubbles, the electrolyte conductivity and temperature, etc. In brief, it was found that reliable and reproducible pulse data could only be obtained if the cell were discharged from one fixed value of the steady load ( $R_s$ ) to another fixed value of the pulse load ( $R_p$ ) for the duration of the discharge capacity of the cell. This is how a battery for an active sonobuoy is employed in practice, so there was merit in adopting a similar procedure for pulse discharging individual cells.

#### PULSE PERFORMANCE OF LEAD CHLORIDE VERSUS SILVER CHLORIDE

Since pulse batteries now in use in active sonobuoys are of the Mg/AgCl type it is of interest to compare the pulse discharge performance of cells having silver chloride and lead chloride cathodes. In Figure 2 a typical comparison is shown for Mg/AgCl and Mg/PbCl<sub>2</sub> cells. As expected the silver chloride cell is superior. The steady discharge output of the AgCl cell was higher, about 1.45 volts versus the Mg/PbCl<sub>2</sub> cell output near 1.0 volts. Both cells were discharged at approximately the same rate in the non-pulsed (or steady drain) mode: 21-25 mA cm<sup>-2</sup> and the load ratio was 18. Although the silver chloride electrode suffered a greater loss of EMF when

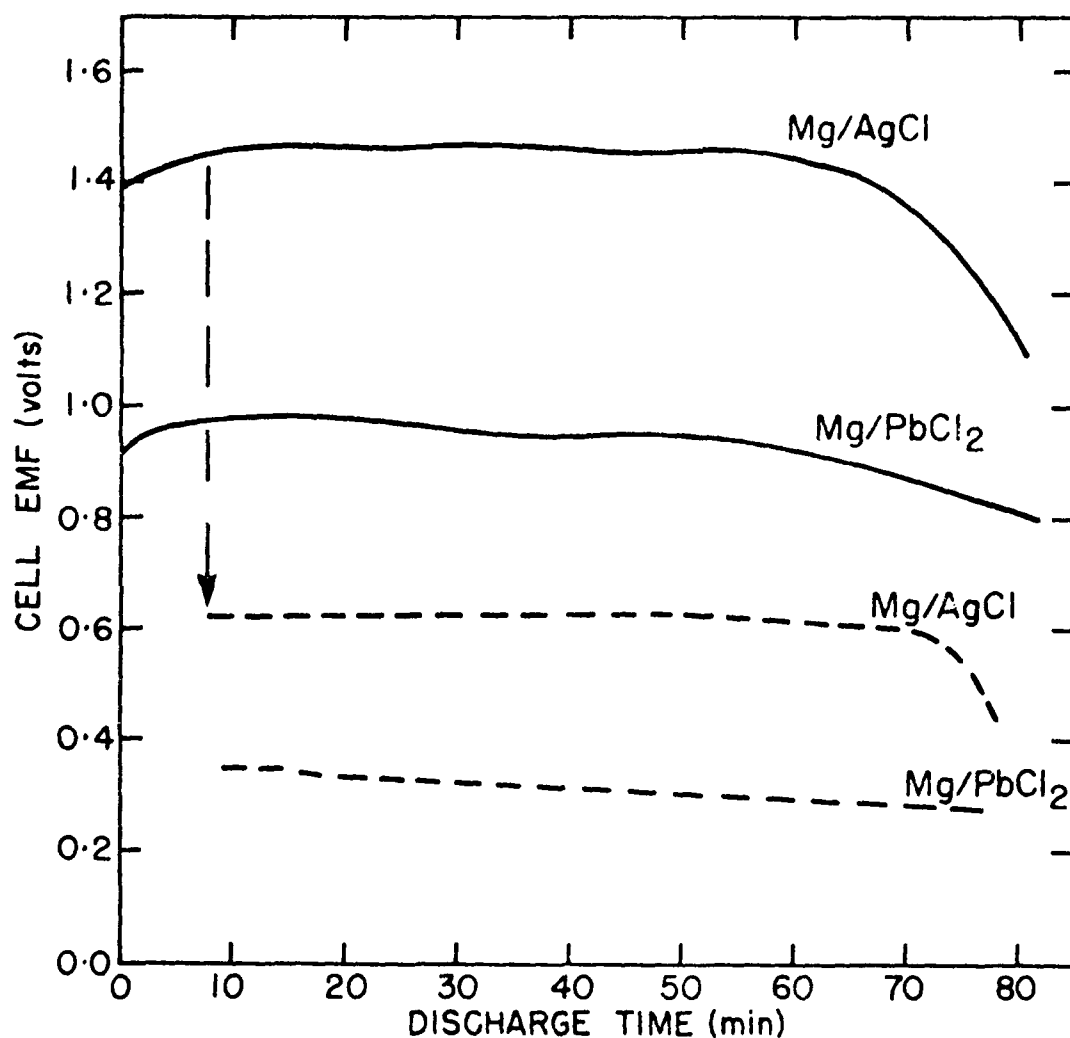


Fig. 2: Comparison of AgCl and PbCl<sub>2</sub> cathodes:

solid curves: "steady" discharge

broken curves: pulse discharge

For Mg/AgCl cell:  $R_s = 0.80 \text{ ohm}$ ,  $R_p = 0.045 \text{ ohm}$

For Mg/PbCl<sub>2</sub> cell:  $R_s = 0.76 \text{ ohm}$ ,  $R_p = 0.042 \text{ ohm}$

pulsed, the pulse voltage of the lead chloride was  $\sim 0.3$  volts lower than for silver chloride. It should also be noted that because the pulse voltage for AgCl was  $\sim 0.6$  volts it was consequently discharging at a higher rate when pulsed than was PbCl<sub>2</sub> whose pulse output fell to  $\sim 0.3$  volts. This is because the pulse loads in both instances were about the same: 0.045 ohm for AgCl and 0.042 ohm for the PbCl<sub>2</sub> cell. In general, the Mg/AgCl cell would be preferred for pulse discharging because of its greater EMF both during steady and pulsed discharge.

### LEAD CHLORIDE CATHODES

#### INFLUENCE OF STEADY DISCHARGE RATE ON PULSE BEHAVIOUR

Several processes occur during the course of discharging a Mg/PbCl<sub>2</sub> cell, but from the aspect of pulse performance the conditions prevailing in the vicinity of the anode are very important. If discharge takes place at a high enough rate the evolution of hydrogen gas due to corrosion of the magnesium will be rapid enough to sustain electrolyte circulation between anode and cathode. The result will be to bring in fresh electrolyte and remove reaction products such as Mg(OH)<sub>2</sub> which could precipitate on the anode or cathode and contribute to an increase in cell resistance. It is reasonable to assume therefore that a minimum critical rate of discharge must be exceeded in order to keep the magnesium and lead chloride surfaces clean and active electrochemically. This factor is especially important when electrical impulses are to be drawn from the cell, because the accumulation of reaction products would diminish the response to the required increase in reaction rate.

In Figure 3 three typical examples are shown in which the discharge rate on steady load was as indicated: 9.6, 16.5 and 19.8 mA cm<sup>-2</sup>. The pulse load was adjusted to provide in each case a similar value of the load ratio. Some of the pertinent data are listed in Table II.

TABLE II

Pulse Discharge of Mg/PbCl<sub>2</sub> Cells  
at Constant Load Ratio

Cell	R <sub>s</sub> (ohm)	R <sub>p</sub> (ohm)	R <sub>s</sub> /R <sub>p</sub>	Mean Steady Rate (mA cm <sup>-2</sup> )	Voltage Drop on Pulse (volts)
A	1.72	0.085	20	9.6	0.58
B	0.94	0.046	20	16.5	0.64
C	0.76	0.042	18	19.8	0.63

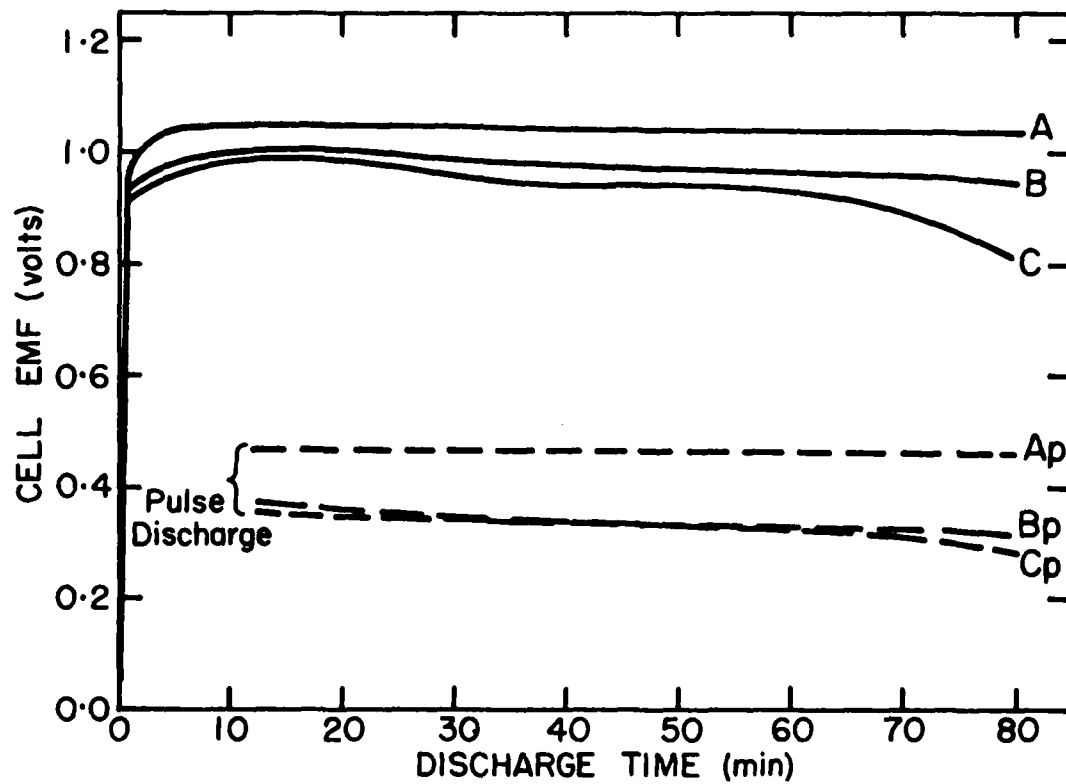


Fig. 3: Influence of "steady" discharge rate on pulse performance.

"Steady" load resistance: A(1.72 $\Omega$ ), B(0.94 $\Omega$ ), C(0.76 $\Omega$ )

Pulse load resistance: Ap(0.085 $\Omega$ ), Bp(0.046 $\Omega$ ), Cp(0.043 $\Omega$ )

Approx. rates at mid-point in "steady" discharge in mA cm<sup>-2</sup>:

A(9.6), B(16.5), C(19.8).



Since the average voltage decrease on pulsing was about the same,  $\sim 0.6$  volts for all three examples it was evident that little advantage was to be gained by having the cell discharge at the higher rate during the steady period. In addition the higher rate would be wasteful of capacity and would contribute to lowering the output voltage delivered during both the steady and pulsed periods. The results of these experiments and preliminary work indicated that the cell response to a pulse drain was acceptable if the steady rate of discharge was kept above approximately  $5 \text{ mA cm}^{-2}$ . Furthermore, there was no practical reason for testing at lower rates, because these would result in excessively large and heavy batteries in order to provide the currents and electrical capacity for the active sonobuoy application.

#### INFLUENCE OF PULSE LOAD ON PULSE BEHAVIOUR

The results of Figure 4 were obtained by pulse discharging  $\text{Mg/PbCl}_2$  cells at various different pulse loads. The steady discharge rate was kept constant at a moderate rate approaching  $\sim 9 \text{ mA cm}^{-2}$  by setting  $R_s = 1.88 \text{ ohm}$ . Values of  $R_p$  were selected so that the load ratio covered as wide a range as possible, this being from  $\sim 10$  to  $\sim 60$ .

In Figure 4 the pulse discharge and steady discharge curves are plotted for six different pulse loads. The individual values of  $R_p$  are given at the right hand side of each pulse curve and the corresponding load ratio has been listed on the left hand side. As mentioned before, pulsing was initiated after approximately 10 minutes of discharge at the chosen steady load ( $R_s = 1.88 \text{ ohm}$ ). In general the average output obtained during a pulse was observed to increase gradually from the onset of pulsing until approximately half-way through the discharge, after which it became almost constant. This effect can be ascribed to such factors as increased activity and development of electrode surface properties and also to changes in electrolyte pH, concentration and temperature. These data best represent the pulse performance of the AIRI  $\text{PbCl}_2$  for the active sonobuoy battery application. It should be noted that the relevant load ratio, 25.6 occurs in Figure 4 between the values  $R_p = 0.087 \text{ ohm}$  and  $R_p = 0.061 \text{ ohm}$ . Employing the AIRI electrode in a pulsing battery one should therefore anticipate a loss in cell output of approximately 0.6 volts when the load ratio is  $\sim 25$ . From the data of Figure 4 the average cell output on pulse load has been plotted as a function of the pulse load and this is given in Figure 5. Here the cell output versus pulse load can be seen to have an almost linear relationship. The information contained in Figure 4 and 5 will be used below to attempt some calculations on the design of an active sonobuoy battery using the AIRI  $\text{PbCl}_2$  cathode.

As mentioned above the pulse load was varied over a wide range so that it included values similar to the internal resistance of the cell. The latter,  $R_i$  is easily calculated from a change in cell EMF,  $\Delta V$  corresponding to a change in cell current,  $\Delta I$ :

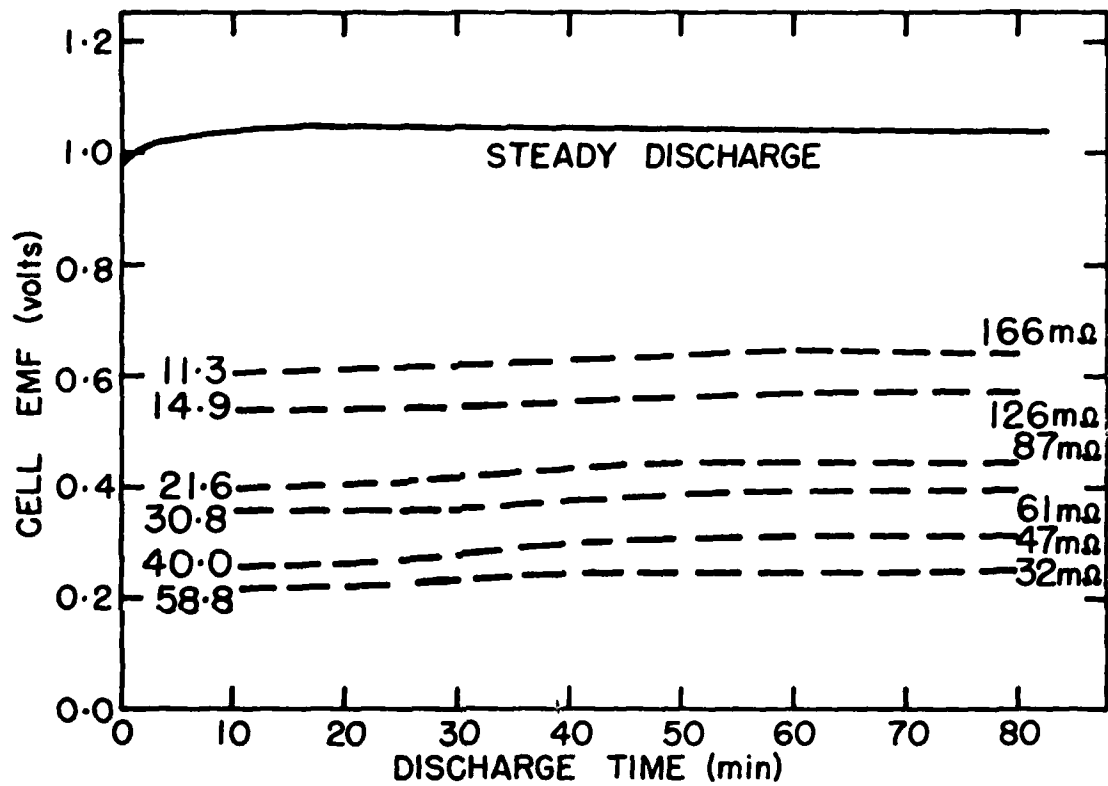


Fig. 4: Effect of pulse load resistance on pulse performance. Solid curve is for "steady" discharge ( $R_s = 1.88\Omega$ ), broken curves for pulse discharge at different load resistances ( $R_p$ ). Figures shown at right side of pulse curves are  $R_p$ , at left side: load ratio ( $R_s/R_p$ ).

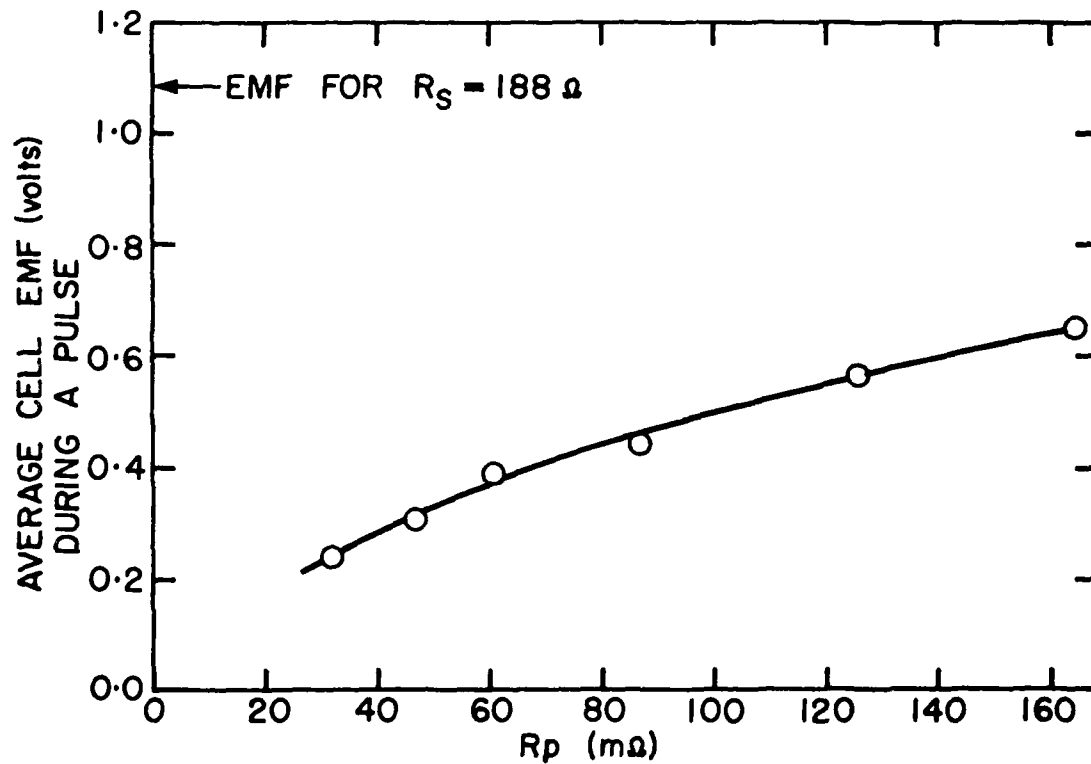


Fig. 5: Pulse performance of  $Mg/PbCl_2$  cells in terms of the average emf delivered during a pulse versus the pulse load resistance,  $R_p$ .

$$R_1 = \frac{\Delta V}{|\Delta I|} = \frac{V_s - V_p}{\left| \frac{V_p}{R_p} - \frac{V_s}{R_s} \right|} \quad [2]$$

In equation [2] the subscript "s" refers to the steady rate of discharge and the subscript "p" to pulse discharge; V is cell output voltage. The value of  $R_1$  (calculated using equation [2]) during the course of a pulsing experiment (some 80 minutes or so) was found to vary with time. It increased initially, going through a maximum some 10-20 minutes after pulsing was started. Thereafter  $R_1$  decreased slowly, levelling out to a constant value for the last 40 minutes of the experiment. These effects were caused by changes in the electrolyte temperature, ionic concentration, pH and accumulation of the products of the cell reaction. There was little novel from the scientific point of view in these observations; for example the final decrease in  $R_1$  can be accounted for by increases in the surface area of the electrodes and the development of the electronically conducting Pb phase over the electronically insulating phase,  $PbCl_2$ . A similar reasoning applied to the increase in pulse EMF observed during the course of discharge (see Figure 4).

It was interesting to note how the internal resistance varied and how its approximate value compared with the applied external load. The output power rose through a maximum for a value of the pulse load which was approximately equal to the measured value of  $R_1$ , found by equation [2]. This type of behaviour is expected (4) and suggests that for optimum efficiency in the pulse application the pulse load should be approximately the same as the internal resistance. For practical reasons, however, it may not be possible to set the pulse load equal to the internal resistance. For instance, in the present situation the required load ratio was 25.6 (see equation [1]) where  $R_p = 0.13$  ohm for maximum power output and  $R_s = 1.88$  ohm (i.e.  $R_s/R_p = 1.88/0.13 = 14.5$ ). In order to obtain a load ratio equal to 25.6 the steady load would have to be  $R_s = 0.13 \times 25.6 = 3.33$  ohms. If 3.33 ohms were used for discharging a cell the steady rate would be less than 5 mA cm<sup>-2</sup> and problems could arise due to cell clogging and a resulting slow response to the pulse as described above.

The shape of the voltage transient underwent some change during a cell discharge. This is shown schematically in Figure 6, where each caption represents the basic shape of the base of the voltage pulse (100 ms in length) at various times as indicated during a typical experimental run. The initial sharp decrease was a switching transient which is inductive, therefore producing a negative-going voltage spike at  $t = 0$ . Following the reorganization of ionic and polar molecular species at the electrode/electrolyte interfaces (i.e. at both anode and cathode) the cell EMF rises through a peak. The gradual decrease during the latter three-quarters of the pulse is due to resistive build-up caused by increased gas evolution and accumulation of other reaction products such as  $Mg(OH)_2$ . As noted in Figure 6 the pulse shape changed most rapidly during the first few pulses. This is due to the relative absence of a porous structure at both electrodes initially, which during the

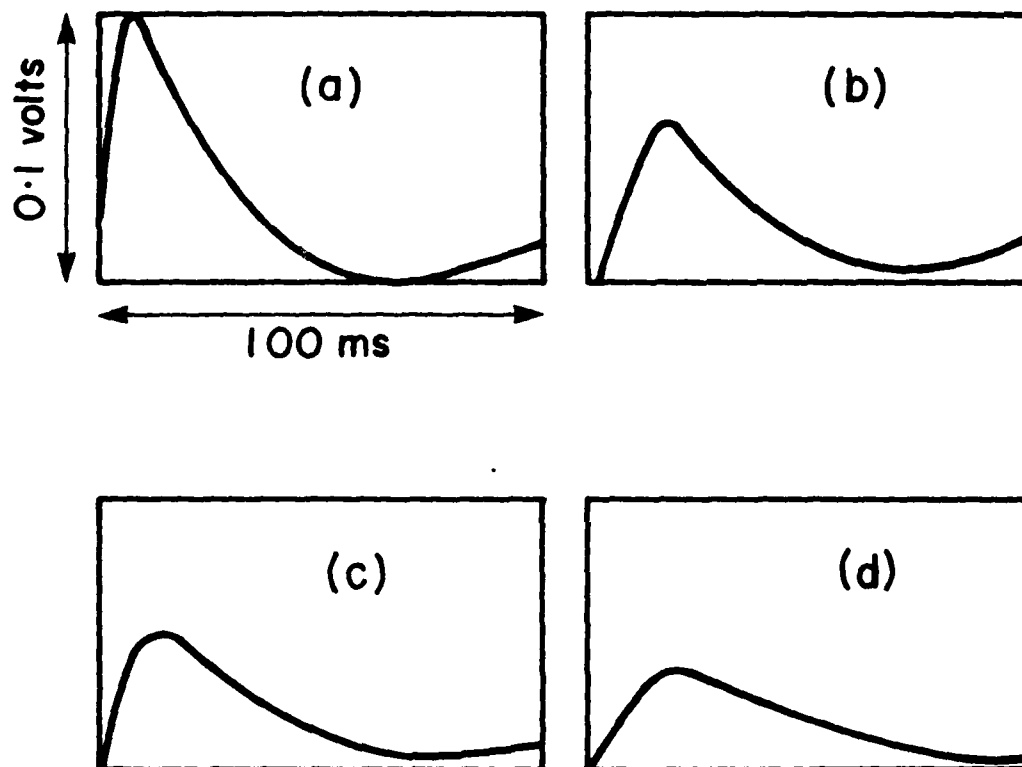


Fig. 6: Typical profile of the voltage at the bottom of the pulse following (a) 1, (b) 20, (c) 35 and (d) 80 minutes of pulsing. Only the lower 0.1 volts of the pulse is shown.

course of subsequent pulsing is developed continuously thereby diminishing cell resistance.

### CONCLUSION

#### DESIGN OF A $\text{Mg/PbCl}_2$ PULSE BATTERY

The experimental work was concluded at this point to analyze the results which had been obtained at ambient temperature using 3.25% aqueous  $\text{NaCl}$  electrolyte. These data are sufficient to permit an estimation of the suitability of the AIRI type of  $\text{PbCl}_2$  cathode for a pulse battery. It will be recalled that the battery was required to produce a nominal 40 volts during steady discharge and to deliver no less than 18.5 volts when pulsed.

The results of the present work will be applied to two examples based upon keeping constant the load ratio,  $R_s/R_p = 25.6$ .

In the first case we choose to discharge at a moderate steady rate by selecting  $R_s = 0.8$  ohm. This will provide an output of about 0.95 volts per cell, as can be estimated from Figure 3. A nominal 40 volt battery would therefore need 42 such cells connected in series. Having set the load ratio, the resulting pulse load is  $R_p = 0.8 \text{ ohm}/25.6 = 0.031$  ohm. From Figure 5 the cell output produced on pulse is consequently 0.23 volts. Thus a 42-cell battery would deliver only about 9.7 volts when pulsed, clearly well short of the minimum 18.5 volts prescribed.

For the second example the steady discharge can be chosen at a lower rate so as to deliver a higher output of 1.04 volts per cell. Therefore let  $R_s = 2.0$  ohm. In this case 39 cells will produce 40.5 volts in keeping with the basic specification calling for 40 volts (nominal). The corresponding value of the pulse load is  $R_p = 2.0 \text{ ohm}/25.6 = 0.078$  ohm and the pulse output taken from the curve in Figure 5 is 0.43 volts. During the pulse discharge the 39-cell battery would produce  $39 \times 0.43 = 16.8$  volts, still somewhat short of the requirement.

In the two cases elucidated above the data indicate that a series arrangement of  $\text{Mg/PbCl}_2$  cells could not meet the voltage minimum required for pulsed operation, even though the steady rate of discharge was allowed to range over a fairly wide spectrum, i.e.  $0.8 \text{ ohm} < R_p < 2.0 \text{ ohm}$ . At lower than ambient temperature the failure would of course be more pronounced.

However, instead of a single string of cells in series, a battery could be designed to place two series strings of cells (e.g. 40 cells each) in parallel. Once again keeping the load ratio of 25.6 the outputs might be as follows:

Steady Discharge

Battery - 40 Mg/PbCl<sub>2</sub> cells in series

$$R_s = 33.3 \text{ ohm}$$

$$V_s \approx 40 \text{ volts}$$

- the unused string of cells would be discharged through a dummy load to keep the electrodes active.

Pulse Discharge

Battery - 2 parallel strings of 40 cells in series

$$R_p \approx 1.3 \text{ ohm (across battery)}$$

$$R_p = 2.6 \text{ ohm (across each 40 cell string)}$$

$$V_p \approx 24 \text{ volts}$$

The obvious conclusion is that the pulse battery specification could be met by the PbCl<sub>2</sub> electrode if a series-parallel configuration is adopted. The main drawback however is the size and weight of such a battery consisting of a total of eighty cells.

In its present state of development the AIRI cathode is too heavy to compete with the silver chloride electrode technology. Silver chloride can be produced in very thin rolled sheets containing about 90% active material, whereas lead chloride made by the AIRI process contains nearly 40% by weight of copper gauze.

Future active sonobuoys will require more compact and efficient power supplies and even Mg/AgCl batteries will be replaced by lithium batteries which offer the advantage of much higher energy density. It is estimated that by 1983 all sonobuoys will be powered by lithium batteries and the seawater-activated battery will be discarded entirely (1).

REFERENCES

1. Consultation with National Defence Headquarters, Director of Avionics and Armament Sub-Systems Engineering - DAASE (4), A.C. Roberts.
2. G.J. Donaldson and J.R. Coleman, "The AIRI Fusion Cast Lead Chloride Electrode; Part I, DREO Technical Note No. 77-16 (1977).

3. G.J. Donaldson and W.D. Barnes, "The AIRI Fusion Cast Lead Chloride Electrode; Part II, DREO Technical Note No. 78-3 (1978).
4. S.U. Falk and A.J. Salkind, "Alkaline Storage Batteries", p. 560, John Wiley and Sons, New York (1969).



UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified

1. ORIGINATING ACTIVITY Defence Research Establishment Ottawa Department of National Defence Ottawa, Ontario, Canada K1A 0Z4	2a. DOCUMENT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP N/A
3. DOCUMENT TITLE PULSE CAPABILITY OF THE AIRI LEAD CHLORIDE ELECTRODE	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) TECHNICAL NOTE	
5. AUTHOR(S) (Last name, first name, middle initial) DONALDSON, George J. and BARNES, William D.	
6. DOCUMENT DATE NOVEMBER 1979 8a. PROJECT OR GRANT NO. 8b. CONTRACT NO.	7a. TOTAL NO. OF PAGES 17 7b. NO. OF REFS 4 9a. ORIGINATOR'S DOCUMENT NUMBER(S) DREO TECHNICAL NOTE NO. 79-26 9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)
10. DISTRIBUTION STATEMENT UNLIMITED DISTRIBUTION	
11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY DAASE
13. ABSTRACT <p>The objective of the study was to evaluate the pulse discharge performance of lead chloride electrodes for the active sonobuoy battery application. Experimental work was carried out using Mg/PbCl<sub>2</sub> cells which were pulse discharged in 3.25% artificial seawater at ambient temperatures (22°-25°C). Pulses of 100 milliseconds duration were applied every ten seconds by switching the cells from their steady discharge load to the pulse discharge load.</p> <p>It was found that the steady rate of discharge had to be maintained at about 5-10 mA cm<sup>-2</sup> in order to permit a sufficiently rapid response to the application of the pulse load without unduly sacrificing electrode capacity. The Mg/PbCl<sub>2</sub> cell was required to accept a pulse load greater than the steady load by a factor of approximately 25; the resulting loss of cell output voltage was about 0.6 volts. Although Mg/AgCl cells suffer about the same loss of output, the levels are about 0.5 volts higher in both steady and pulsed discharge modes than those for the Mg/PbCl<sub>2</sub> cell.</p> <p>A further serious disadvantage of the PbCl<sub>2</sub> electrode is its greater size and weight compared to silver chloride. Lead chloride electrodes do not offer a performance advantage over silver chloride for active sonobuoy batteries. In view of the impending conversion of all types of sonobuoys to the use of lithium batteries in about five to eight years time there is little advantage to pursuing the development of the lead chloride electrode for such applications.</p>	

# UNCLASSIFIED

Security Classification

## KEY WORDS

SONOBUOY BATTERIES  
WATER ACTIVATED BATTERIES  
PULSE DISCHARGE  
LEAD CHLORIDE

## INSTRUCTIONS

1. ORIGINATOR'S ACTIVITY. Enter the name and address of the organization issuing the document.
- 2a. DOCUMENT SECURITY CLASSIFICATION. Enter the overall security classification of the document, including special warning terms, whenever applicable.
- 2b. GROUP. Enter security reclassification group number. The three groups are defined in Appendix A of the DIRM Security Regulations.
3. DOCUMENT TITLE. Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one capital letter abbreviation in parentheses immediately following the title.
4. DESCRIPTIVE NOTES. Enter the category of document, e.g. technical report, technical note or technical letter. If appropriate, enter the type of document, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.
5. AUTHOR(S). Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.
6. DOCUMENT DATE. Enter the date (month, year) of Establishment approval for publication of the document.
- 7a. TOTAL NUMBER OF PAGES. The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. NUMBER OF REFERENCES. Enter the total number of references cited in the document.
- 8a. PROJECT OR GRANT NUMBER. If appropriate, enter the applicable research and development project or grant number under which the document was written.
- 8b. CONTRACT NUMBER. If appropriate, enter the applicable number under which the document was written.
- 9a. ORIGINATOR'S DOCUMENT NUMBER(S). Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.
- 9b. OTHER DOCUMENT NUMBER(S). If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).
10. DISTRIBUTION STATEMENT. Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as:
  - (1) "Qualified requesters may obtain copies of this document from their defence documentation center."
  - (2) "Announcement and dissemination of this document is not authorized without prior approval from originating activity."
11. SUPPLEMENTARY NOTES. Use for additional explanatory notes.
12. SPONSORING ACTIVITY. Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.
13. ABSTRACT. Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (S), (C), (R), or (U).  
  
The length of the abstract should be limited to 20 single-spaced standard typewritten lines; 7 1/4 inches long.
14. KEY WORDS. Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context.